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A NEW SYNTHESIS OF C¹⁴ LABELED CYANIDE¹

BY J. W. SPYKER AND A. C. NEISH

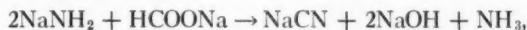
ABSTRACT

Sodium formate was converted to sodium cyanide in high yields, usually better than 85%, by heating with two molecular proportions of sodium amide at 620°C. for 12 min. in a stainless steel bomb. A modified synthesis of sodium formate, from the carbon-14 sodium carbonate solution supplied commercially, is described, yield 95-97%.

The methods developed for the synthesis of radioactive sodium cyanide all have certain inherent disadvantages. The reduction of carbon dioxide with ammonia and potassium (5) gives yields of 90 to 96%; however, the procedure is tricky and time-consuming, as well as being limited to a scale of about one millimole. The reduction of barium carbonate with sodium azide (1) gives maximum yields of about 78%, but the nature of the barium carbonate crystals is critical, and explosions are often encountered (4) unless extreme precautions are taken. A recent procedure (2) has the advantage of not requiring high temperature and pressure, but the yields are reduced to 68-72% because of the long series of reactions necessary. The present investigation was completed before the promising method of McCarter (6) came to our attention.

The ease of preparation of sodium formate from sodium carbonate suggested its use as an intermediate in the synthesis of cyanide. Several reactions for conversion of formate to cyanide were investigated. An exchange reaction between adiponitrile and formic acid gave only 2.1% hydrogen cyanide after three hours at 300°C. Sodium formate was heated with phospham (8) in a stream of nitrogen; the yields of cyanide varied, with a maximum of 35%.

It was found that sodium formate reacted with sodium amide, probably according to the equation



to give yields of cyanide as high as 93% with an average yield of 85% under optimum conditions. These conditions were found to be a two to one molar ratio of sodium amide to sodium formate, and a reaction time of 12 min. at 620°C. in a sealed stainless steel bomb. The molar ratio of reactants and the temperature had a marked effect on the yield, as can be seen from Tables I and II. The time of heating had a small effect, with 12 min. being about the optimum. When C¹⁴ labeled formate was used the activity yield was equivalent to the material

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yield. A sample of sodium amide prepared in the laboratory gave good yields of cyanide only when three moles of it was used per mole of formate.

Some experiments were carried out using an evacuated, sealed Pyrex tube in place of a stainless steel bomb. These gave some satisfactory results but the quantities of reactants were severely limited because of the high pressures reached during the reaction. For example, with a reaction tube of about 11.5 cc. volume the maximum amounts of sodium formate and sodium amide that could be used safely were 60 to 70 mgm. and 130 to 140 mgm. respectively.

This synthesis has several advantages over previous methods. It can be carried out rapidly and the techniques involved are straightforward. Sodium amide is available commercially and C^{14} labeled sodium formate can be prepared readily and stored without danger of decomposition. The over-all yield of 82-88% during the conversion from C^{14} -sodium carbonate to C^{14} -sodium cyanide compares favorably with other methods.

EXPERIMENTAL

Methods and Materials

The sodium amide was obtained from Farchan Chemical Laboratories. The inactive sodium formate was prepared by neutralizing Anachemia Chemicals Limited 98-100% formic acid with carbonate-free sodium hydroxide to the phenol red end point, treating with charcoal to remove the indicator, filtering, and evaporating at 100 to 110°C. Cyanide was determined by the standard argentimetric method (9).

Preparation of C^{14} -Sodium Formate

This is essentially the method of Melville, Rachele, and Keller (7) but has been simplified considerably. We have found that sodium bicarbonate gives as good yields as potassium bicarbonate, contrary to statements in the literature (3).

An aliquot of the solution of C^{14} -sodium carbonate in 0.5 *N* sodium hydroxide (as purchased from Eldorado Mining and Refining (1944) Ltd.) containing 100 microcuries was treated with sufficient sodium bicarbonate to give two millimoles and titrated with inactive formic acid to the bicarbonate end point using meta-cresol purple as indicator. The solution was transferred to a glass bomb liner using sufficient water to make 20 ml., treated with 2 ml. of a 6% suspension of palladium black (prepared by reducing palladium chloride with alkaline formaldehyde at 4 to 8°C.), and hydrogenated for 24 hr. at 80°C. at a pressure of 3700 lb. per square inch. The catalyst was filtered out, the solution acidified with inactive formic acid, and the carbon dioxide swept out by carbon dioxide-free air. The solution was then neutralized with sodium hydroxide to the phenol red end point, treated with charcoal, filtered, and the filtrate evaporated to dryness on a steam bath.

The yield of formate from bicarbonate was 95 to 97% in the three experiments tried, as measured by dichromate oxidation or titration of the total acids extracted by ether.

Description of Bomb

Bomb *A* in Fig. 1 was the type used for the results reported in Tables I and II. The cap *D* and the bomb *F* were turned from stainless steel 316 rod, and the gasket *E* was cut from 21 gauge gold sheet. The bomb volume was 2 ml. The external dimensions of the bomb were not critical since the rather slow heating and cooling periods maintained temperature conditions approaching equilibrium. Gold was found to be more satisfactory than copper as a gasket material owing to greater malleability and reduced chemical reactivity.

Bomb *B* in Fig. 1 is of later design. Several reactions at optimum conditions have been performed and gave yields comparable to those obtained with Bomb *A*. The bomb *Z*, plug *X*, cap *W*, and cap screw *V* were turned from stainless steel

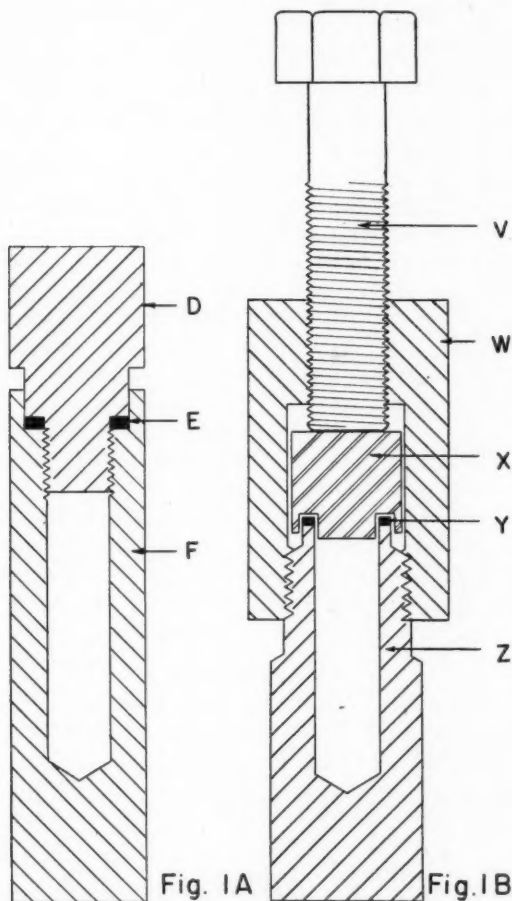


FIG. 1. Two types of bombs used in cyanide synthesis.

TABLE I
THE EFFECT OF MOLAR RATIO OF REACTANTS ON YIELD
All experiments run at 620°C. for 12 min.

Experiment No.	Molar ratio, $\text{NaNH}_2 : \text{HCOONa}$	Yield of NaCN, %
1	2.7:1	44.8
2	2.3:1	62.8
3	2.0:1	86.5
4	2.0:1	83.6
5	1.9:1	88.5
6	1.8:1	82.8
7	1.6:1	76.4
8	2.0:1	86.0*

* C^{14} -sodium formate was used.

316 rod, and the gasket *Y* was cut from 21 gauge gold sheet. The bomb volume was 2 ml. This design is superior to Type *A* in that none of the reaction melt can reach the threads and hence danger of sticking and loss of reaction mixture is lessened.

Reaction of Sodium Amide and Sodium Formate

The bomb (Fig. 1*A*) was flushed with anhydrous ammonia and 360 ± 5 mgm. sodium amide was added with a scoop of suitable size. An accurately weighed amount of sodium formate was added, the bomb was again flushed with ammonia and sealed, care being taken not to mix the reactants. The bomb was placed in a tubular electric furnace and the temperature raised from room temperature to the reaction temperature. This temperature was maintained for the desired time. The bomb was allowed to cool to 400°C. in the furnace, then removed and allowed to cool to room temperature.

The bomb was opened, the melt rinsed into a 125 ml. boiling flask with successive portions of water, and the total volume made to 50 ml. The flask was connected to a condenser, the outlet of which led below the surface of about 30 ml. of solution containing a slight excess of sodium hydroxide. Seven or eight milliliters of 10 *N* sulphuric acid was added to the distillation flask through a dropping funnel and the hydrogen cyanide steam distilled until 40 to 45 ml. of distillate was obtained. It was then analyzed by the argentimetric method (9). The results obtained are shown in Tables I and II.

TABLE II
THE EFFECT OF REACTION TEMPERATURE ON YIELD

A 2:1 molar ratio of sodium amide to sodium formate was used in all experiments; heated for 12 min. at the temperature indicated.

Experiment No.	Temperature, °C.	Yield of NaCN, %
1	570	64.4
2	595	79.0
3	620	83.8
4	645	81.4
5	670	64.6

Procedure Recommended for Preparation of $NaC^{14}N$

Some recent experiments using the optimum conditions in Tables I and II have given yields of 88.0, 92.5, and 93.7%. After flushing with dry ammonia the sodium formate (5 mM.) was added first and then the sodium amide (10 mM.) without mixing. The bomb was opened by loosening screw *V*, and unscrewing cap *W*. After the cap *W* was completely unscrewed, but before it was removed, it was raised slightly and then twisted sideways to pry off the plug *X*. Since *X* was usually stuck the sudden release of pressure propelled it up inside *W* with a noise like a rifle shot. However, there was little or no shock and this operation is quite safe if carried out as described. The sodium cyanide was extracted with water and purified by distillation as described in the preceding paragraph. It is very important to be careful not to do anything which will spread the reactants over too much of the internal surface of the bomb. If it is shaken after sealing a deep blue compound (presumably Prussian blue) is formed during distillation with a marked reduction in the yield of hydrogen cyanide to about 40-60%. A similar result is obtained if the bomb is heated in a vertical position, probably owing to "bumping" of the mixture.

We wish to acknowledge the valuable technical assistance of Mr. M. D. Chisholm, particularly in the design and fabrication of the bomb.

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THE REACTION OF PYRIDINE AND PICOLINES WITH 2-BROMO-2-NITRO-1,3-INDANDIONE¹

BY STEPHEN J. METRO² AND ALFRED TAURINS

ABSTRACT

2-Bromo-2-nitro-1,3-indandione (I) reacts with pyridine in a complex reaction at ordinary temperature. The main reaction products are 2-nitro-1,3-indandione pyridine salt, pyridine hydrobromide, phthalic acid, and a black tar consisting of oxidized polymer of pyridine hydrobromide. The reaction of (I) with picolines follows the same route.

The electronic theory has been applied to demonstrate the structure of 2-nitro-1,3-indandione (II). In water solutions or in salts (II) exists in the form of an anion which is stabilized by several resonating structures.

INTRODUCTION

As a part of the investigation of the action of certain bromoketo compounds and pyridine we studied the reaction of 2-bromo-2-nitro-1,3-indandione (I) with pyridine, and α -, β -, and γ -picolines. The main objective of this work was to elucidate the reactivity of bromine atom in (I).

(I), a white crystalline compound, was prepared by G. Wanag (9, 10) by bromination of 2-nitro-1,3-indandione (II) in water solution. Although (I) could reveal great reactivity toward organic substances, only the reaction of it with sodium iodide, and various hydrolytic agents such as water, dilute sulphuric acid, and sodium hydroxide solution, has been studied (11). (I), when allowed to react with water or 0.2*N* sodium hydroxide solution, gave (II) and hypobromous acid. Dilute sulphuric acid hydrolyzed (I) to phthalic acid and bromonitromethane. (I) showed a characteristic behavior toward sodium iodide in that it oxidized iodide to free iodine. This reaction is also given by α -bromoketones (6), and other organic compounds containing positive bromine (13, 14). The thermal decomposition of (I) in nitrobenzene to yield 2,2-dibromo-1,3-indandione and ninhydrin (10) is one of the most significant reactions of (I). Allen and Wilson (1) indicated that this process may give a clue to the reaction mechanism of bromonitro compounds with other substances. As the first step this mechanism involves the elimination of the nitro group and bromine atom which form active oxygen atoms and nitrosylbromide. In this regard bromonitro compounds differ from other compounds containing "positive bromine"; for example, *N*-bromo-succinimide reacts under elimination of bromine atoms only (14).

DISCUSSION

(I) reacted with pyridine at room temperature to form light yellow crystals which separated from excess of pyridine. These crystals were identified as 2-nitro-1,3-indandione pyridine salt (IV). Only a very small amount of unreacted (I) could be separated by ether extraction of the solid fraction of the reaction mixture.

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Contribution from the Organic Chemistry Laboratory, McGill University, Montreal, Que. Presented before the Summer Seminar in the Chemistry of Natural Products, University of New Brunswick, Fredericton, N.B., July 12, 1951.

² Present address: Esso Research Laboratories, Standard Oil Development Company, Linden, N.J.

The pyridine solution was kept for seven days in a stoppered flask during which time pyridine hydrobromide precipitated in crystalline form. After the removal of these crystals the mother liquid was separated by fractional distillation at reduced pressure into three fractions: pyridine, phthalic anhydride, and a very small amount of a colorless lachrymatory liquid, probably bromonitromethane. The residue which did not distill was a black tar which contained both nitrogen and bromine, and in aqueous solution gave an immediate precipitate of silver bromide with silver nitrate.

A black tar was always a reaction product of the bromination of pyridine and was ignored for the most part by the workers in this field. McElvain and Goese (5) proposed an oxypyridyl type structure for such a type of polymer. A complete elementary analysis (C-H,N,Br) of the black tar which was obtained in our work amounted to 89% (the remaining 11% assumed to be oxygen). Therefore it differed from McElvain-Goese's compound. The fact that it was a hydrobromide salt of a pyridine derivative was shown by the reaction of sodium hydroxide solution on the black tar, namely, a substance of pyridine like odor was liberated. For the black tar the formula (III) can be proposed in which the pyridine nuclei are joined by oxygen.

Starting from 14 gm. (0.052*M*) of (I) and 17 gm. (0.2 *M*) of pyridine the following products were obtained in the amounts indicated:

- 4.5 gm. of 2-nitro-1,3-indandione pyridine salt (IV),
- 3.1 gm. of pyridine hydrobromide,
- 0.1 gm. of the lachrymatory liquid,
- 1.24 gm. of phthalic anhydride corresponding to 1.1 gm. of phthalic anhydride,
- 4.8 gm. of the black tar, and 0.1 gm. of the unreacted (I).

The starting material (I) contained 4.15 gm. of bromine and the total bromine content of the products was about 2.91 gm. The loss of bromine was 1.24 gm. (30%). It was observed during the reaction of (I) with pyridine that starch-iodide paper inserted in the neck of the flask turned dark blue. This indicated that bromine or nitrosylbromide was given off during the reaction. This gas evolution would account for the loss of bromine in the reaction.

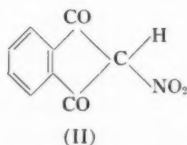
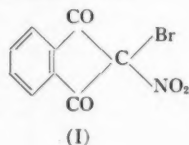
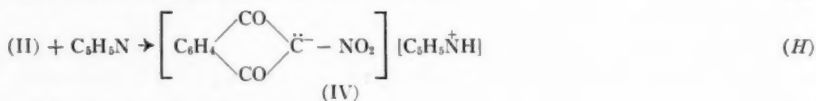
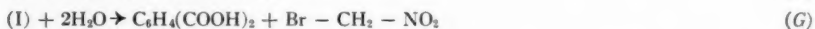
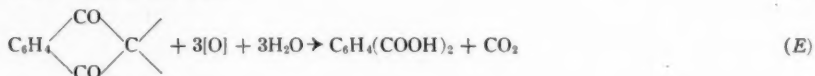
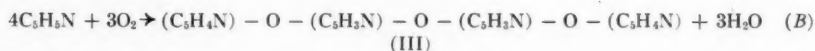
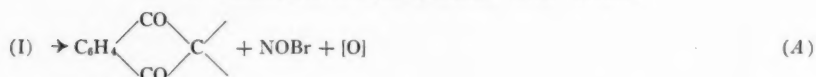
The three picolines (α -, β -, γ -) reacted with (I) at ordinary temperature to give 2-nitro-1,3-indandione picolinium salts as the main reaction products. The reaction of β -picoline is considerably slower than the reactions of α - or γ -picoline with (I).

It would be possible to write a series of equations (A - K) which would account for the various products formed in the reaction of pyridine with (I) considering the behavior of (I) in the reactions of hydrolysis (11) and thermal decomposition (10). These equations do not necessarily represent the only possible mechanism, but they follow routes suggested by known reactions of bromonitro compounds.

To account for the fact that (I) forms (II) in the reaction with pyridine it is necessary to assume a series of reactions which involve formation of water. Water could be formed only by oxidation of pyridine hydrogen atoms by oxygen

produced by the interaction of nitro group and bromine atom (*B*). The group of equations explains the formation of phthalic acid, bromonitromethane, as well as (II) which forms the main reaction product, 2-nitro-1,3-indandione pyridine salt (IV). The hydrogen bromide needed for the formation of the two salts (Equations *D* and *K*) could arise from hydrolysis of nitrosylbromide or from hypobromous acid.

SCHEME I
REACTION MECHANISM
OF 2-BROMO-2-NITRO-1,3-INDANDIONE WITH PYRIDINE

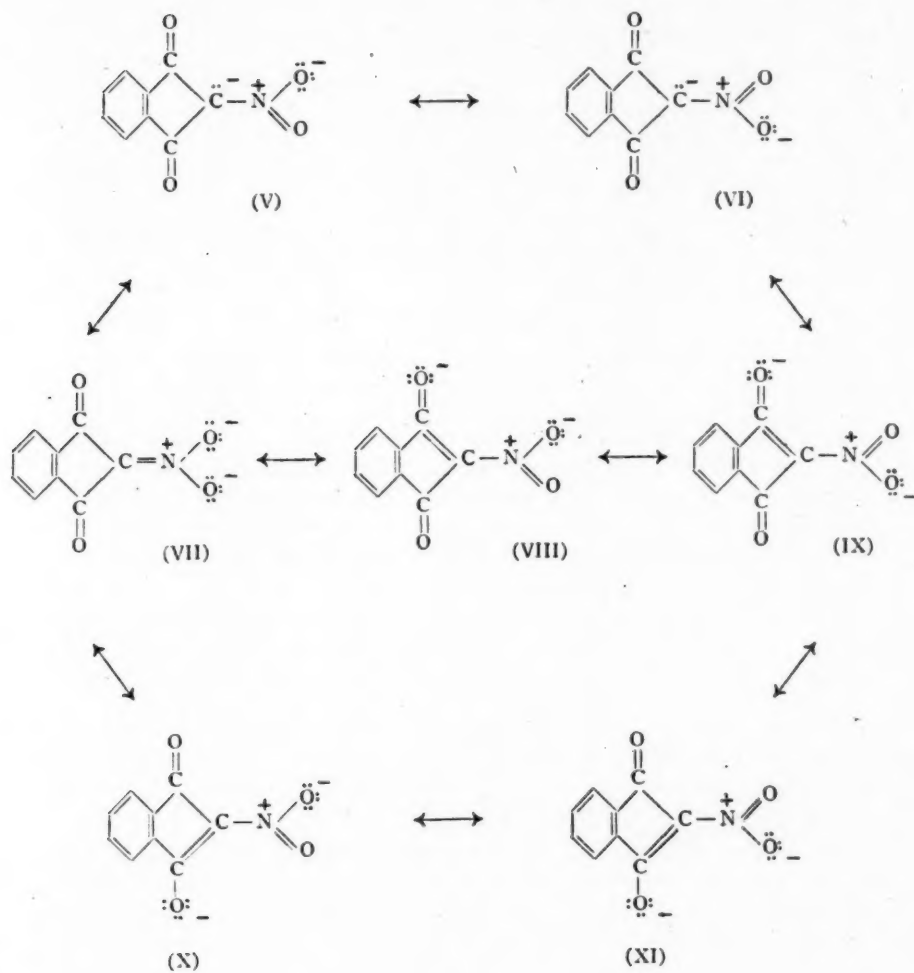


The Electronic Structure of 2-Nitro-1,3-indandione

G. Wanag found that (II) is a strong acid and can serve as a very useful reagent for precipitation and identification of various amines and alkaloids (9). This reagent is now available commercially from Pierce Chemical Company, Rockford, Ill., and references to its use are given by Christensen, Wang, Davies, and Harris (4). The structure of (II) has been known only incompletely. On the basis of titration of (II) with bromine, G. Wanag and J. Bungs (11) concluded that in water solution (II) does not exist as a nitro ketone but as the aci-nitro form.

It is generally known that primary and secondary nitro compounds do not give the color reaction with ferric chloride (12) unless they have been dissolved in a base and regenerated by acidification of the basic solution. We could confirm

SCHEME II
 RESONANCE HYBRID STRUCTURE OF THE 2-NITRO-1,3-INDANDIONE ANION



the validity of this rule for (II). This fact indicates that in water solution (II) does not exist in the aci-nitro form. The explanation of the reactivity of (II) may be obtained by assigning the resonance hybrid structure (V-XI) to the anion which may be formed in the process of dissociation of (II). These resonance structures are advanced on the basis of the modern views on carbanion keto-enol and nitro-aci-nitro structures (2, 3, 8, 12). Two of these structures (V and VI) are of the carbanion type, one (VII) is an aci-nitro anion structure, and four (VIII, IX, X, and XI) are enolate structures. The dissociation of (II) in water solution to form a strong acidic medium is determined by the permanent polarization of two carbonyl, and a nitro group of the (II) molecule, and the resonance stabilization of the anion (V-XI). Bromination and salt formation of (II) may proceed through these resonance structures as well.

The effect of permanent polarization by the carbonyl groups is responsible for the reactivity of (I) by its bromine atom and nitro group.

EXPERIMENTAL

2-Bromo-2-nitro-1,3-indandione (I) was prepared by bromination (9, 10) of 2-nitro-1,3-indandione which was obtained from the Pierce Chemical Company, Rockford, Ill. We found that the yield of (I) was only about 68.5%. The previously claimed (10) yield of 98% of (I) was probably a result of erroneous calculations. In all bromination reactions of (II) we found certain amounts of phthalic acid which could arise from the acidic hydrolysis of (I) and which accounted for the lower yields. Pyridine and picolines which were used for this work were dried over barium oxide and distilled from potassium hydroxide.

Reaction of Pyridine with (I) at Room Temperature

To 14 gm. (0.052 M) of (I), 15.8 gm. (0.2 M) of pyridine was slowly added, with stirring, in nitrogen atmosphere at room temperature. The solution turned yellow in color and some yellow solid material precipitated. The reaction flask was placed in the refrigerator overnight, after which the solid was removed by filtering and extracted with ethyl ether in a Soxhlet extractor. The filtrate (liquid A) was allowed to stand one week in a stoppered flask. This extraction process gave an ether insoluble fraction (A) and an ether soluble fraction (B).

2-Nitro-1,3-indandione Pyridine Salt (Fraction A) (IV)

This portion was a yellow crystalline product which after several recrystallizations from ethanol had a very fine platelike form and melted at 169-170° with decomposition. Crystallization from water gave large transparent crystals of the same melting point. A mixed melting point with a sample of pyridine salt prepared from (II) and pyridine gave no depression.

Anal. Calcd. for $C_{14}H_{10}O_4N_2$: C, 62.23; H, 3.70; N, 10.38%.

Found: C, 62.27; 62.20; H, 3.99; N, 10.33; 10.29%.

Fraction B (I)

The ether was distilled off the ether soluble fraction. The product which remained, (I), was recrystallized twice from ethanol and obtained as a white

microcrystalline solid, m.p. 111-112°; the yield of (I) was 0.1 gm. A mixed melting point with an authentic sample of (I) showed no depression.

Anal. Calcd. for $C_9H_4O_4NBr$: C, 40.02; H, 1.49%. Found: C, 40.31; H, 1.65%.

Pyridine Hydrobromide

After crystals of 2-nitro-1,3-indandione pyridine salt had been removed by filtration from the reaction mixture the liquid A was allowed to stand for a week at room temperature. During this time the solution turned dark and some light brown colored crystals precipitated. The yield of a crude product was 2.2 gm. Early attempts to recrystallize these crystals were unsuccessful because of their extreme solubility in polar solvents and their insolubility in nonpolar solvents. Finally it was observed that the substance could be recrystallized from 1,3-dibromopropane. Pyridine hydrobromide was obtained as pure white powder, m.p. 207-209°.

Anal. Calcd. for C_5H_6NBr : Br, 49.93%. Found: Br, 50.02%.

Pyridine hydrobromide was transformed into a pyridine picrate in the form of bright yellow crystals, m.p. 163-164°.

Anal. Calcd. for $C_{11}H_8O_7N_4$: C, 43.00; H, 2.28; N, 18.18%. Found: C, 43.58; H, 2.72; N, 18.00%.

Phthalic Anhydride

The dark brown pyridine solution which remained after the removal of pyridine hydrobromide was distilled. After the pyridine was distilled off, white needles of phthalic anhydride began to form in the neck of the distilling flask (at 28-32° and 0.3 mm. Hg pressure). At 33-40° and 0.3 mm. approximately 0.1 ml. of a colorless liquid came over and a black tar remained in the distilling flask. The phthalic anhydride was purified by sublimation under reduced pressure and recrystallization from ethanol. The yield was 1.1 gm. It was identified by elementary analysis, derivatives (phthalimide, phthalic acid, and phenolphthalein), and m.p. 129-130°.

Anal. Calcd. for $C_8H_4O_3$: C, 64.81; H, 2.70%. Found: C, 64.50; H, 2.81%.

The Black Tar (III)

The black tar which remained in the distillation flask could not be distilled or recrystallized. It was quite soluble in water and ethanol.

Anal. Calcd. for $C_{20}H_{16}O_3N_4$: C, 46.2; H, 3.08; N, 10.08; Br, 30.08%. Found: C, 44.5; 44.3; H, 3.55; 3.24; N, 10.15; 10.10; Br, 32.8; 30.9%.

Bromonitromethane

The lachrymatory liquid which came over at the final distillation was a colorless liquid of very sharp odor. It contained both bromine and nitrogen but did not give a picrate. It was not obtained in an amount sufficient to analyze quantitatively. The micro boiling point determination gave the value of 140-145° which is close to the boiling temperature (147.5-149.5° at 742 mm.) of bromonitromethane reported in the literature (7).

Reaction of (I) with Alpha-, Beta-, and Gamma-picoline

To 2 ml. of freshly distilled α -picoline 0.5 gm. of (I) was added. The solution turned yellow immediately and the main reaction product, 2-nitro-1,3-indandione

α -picoline salt, formed within a few minutes as a yellow crystalline compound. The salt was recrystallized from ethanol; the melting point was 160-161° (decomp.). A mixed melting point with an authentic sample of this salt showed no depression.

β -Picoline reacted with (I) to give 2-nitro-1,3-indandione β -picoline salt. After recrystallization from ethanol it had the melting point 145-146° (decomp.).

The corresponding γ -picoline salt was obtained by a similar procedure. This salt was recrystallized from ethanol and melted at 172-173° (decomp.). An authentic sample of the 2-nitro-1,3-indandione γ -picoline salt was prepared and had the same melting point. The above mentioned picoline salts were reported by Christensen and his co-workers (4) and in most instances his values were lower than the values reported in this paper.

ACKNOWLEDGMENT

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THE FORMATION OF TRIFLUOROMETHYL RADICALS IN THE GAS PHASE¹

By J. W. HODGINS² AND R. L. HAINES³

ABSTRACT

Trifluoromethyl radicals were produced by the reaction between atomic sodium and iodo-, bromo-, and chloro-trifluoromethane in the diffusion flame apparatus. The results indicate that:

- (1) The primary reaction is $\text{CF}_3\text{X} + \text{Na} \rightarrow \text{NaX} + \text{CF}_3$.
- (2) For the reaction between sodium and iodo-, bromo-, and chloro-trifluoromethane, the activation energy is 1.7, 2.3, and 7.4 kcal. per mole, respectively.
- (3) Some decomposition of trifluoromethyl radicals occurs, yielding chiefly tetrafluoroethylene.
- (4) Reaction occurs between molecular hydrogen and trifluoromethyl radicals yielding fluoroform.

INTRODUCTION

The energy necessary to rupture the first carbon-fluorine bond in carbon tetrafluoride has been shown by photochemical experiments to exceed 154 kcal. per mole (5). However, there is reason to suspect that the second C-F bond is quite a weak one—that is, that the trifluoromethyl radical is thermally unstable. Since the highest estimate of the average bond energy in carbon tetrafluoride is about 123 kilocalories per mole, the strength of some of the bonds remaining after the first fluorine atom has been removed must be considerably lower. And the fact that Dacey and Hodgins (5) found no hexafluoroethane in the products of the xenon photosensitized decomposition of carbon tetrafluoride indicates that it may be the CF_3 radical which is unstable.

It was of interest, therefore, to produce CF_3 radicals in the gas phase; this was accomplished by the action of atomic sodium on iodotrifluoromethane in the sodium diffusion flame apparatus so frequently used for comparing the reactivities of organic halides. Since the carbon-iodine bond is such a weak one it was felt that the sodium atoms would react predominantly with the iodine atom, leaving a CF_3 fragment. As the experiments progressed, the reactions between sodium atoms and bromo- and chloro-trifluoromethane were also studied.

APPARATUS AND TECHNIQUES

The apparatus used for producing trifluoromethyl radicals was similar to that described by Hodgins, Tickner, and LeRoy, in a paper on the applications of atomic sodium reactions (7). The changes made were mainly in the design of the reactor, and the method of measuring the partial pressure of the halide reactant. The apparatus is illustrated in Fig. 1.

A vertical reactor was employed in order that the solid deposits formed on the reactor wall could be easily leached out for analysis. The furnace, shown by

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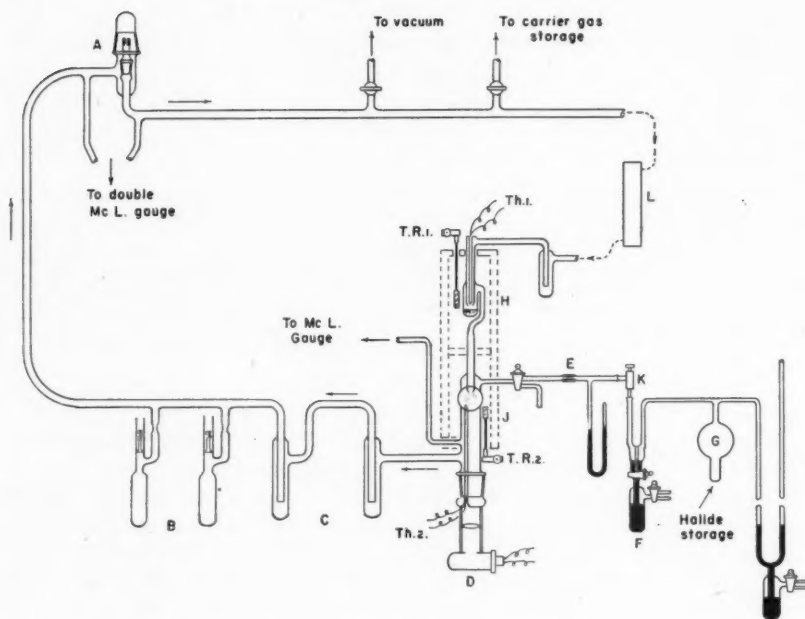


FIG. 1. Diffusion flame apparatus.

dotted lines, was divided into two separately controlled sections, *H* and *J*, so that the carburetor temperature could be altered independently of the temperature of the reaction zone. The bimetallic thermoregulators T.R.1 and T.R.2 held each section of the furnace to within $\pm 0.3^\circ\text{C}$. of the required temperature, and thermocouples Th.1 and Th.2 were used to measure the sodium temperature and the reaction temperature respectively. The reaction zone was illuminated from below by the sodium lamp, *D*.

In operation of the apparatus, carrier gas at about 2-3 mm. pressure was circulated at a high rate by a mercury diffusion pump (represented by *L*), and impinged upon the sodium in the carburetor, where it became saturated with sodium vapor in the atomic state, at the temperature of the upper furnace *H*. The sodium-saturated carrier gas emerged from the 3 mm. jet into the reaction space, where it met an atmosphere of the halide, which was allowed to flow in at an appropriate rate controlled by needle valve *K*, from the calibrated storage volume, *G*.

The partial pressure of the halide was controlled so that the fluorescing zone (consisting of unreacted sodium atoms) was a sphere about 2.0 cm. in diameter. By previous experiments, it was found that in this apparatus, the fluorescence of the sodium vapor becomes invisible at a partial pressure (P_0) of sodium of 2×10^{-5} mm. The unreacted halide and lower-boiling products of the reaction between the halide and the sodium were condensed in the traps, *C*, refrigerated

by liquid nitrogen. The carrier gas, along with any noncondensable products of reaction, was metered by the pressure drop across orifice *A*, whose dimensions are known. A double McLeod gauge was used for measuring the differential. After passing through the metering orifice, the carrier gas re-entered the circulating pump and began the cycle again.

When the experiment had been carried on for a sufficiently long period, the supply of halide was stopped, and the carrier gas allowed to circulate for about 15 min. longer to ensure that all the condensable products had been swept into the traps *C*. A sample of the carrier gas was taken for analysis by means of a Toepler pump, and the remaining carrier gas pumped out. The condensable products were then distilled *in vacuo* into one of the bulbs *B* refrigerated in liquid nitrogen. When all of the condensable products were contained in bulb *B*, the bulb was sealed off with the torch, and removed from the apparatus, which could then be used for the next run, while the reaction products were being analyzed.

Two carrier gases were employed—hydrogen and helium. The hydrogen was purified by admitting it to the system through a hot palladium thimble; the helium, supplied by Dr. W. G. Schneider of the National Research Council, had been specially purified of hydrogen and nitrogen, and its purity checked on the mass spectrometer.

Analytical Procedure

(a) Noncondensable Products

The products of the run which would not condense in the liquid nitrogen trap were sampled by means of a Toepler pump, and stored over mercury in a small glass bulb, of the size required for use on the Blacet-Leighton micro gas analysis apparatus (2). In all of the runs in which hydrogen was used as the carrier gas, negligible quantities of impurities were discovered, and it was assumed from this that all of the products of the reaction were condensable at liquid nitrogen temperature at the operating pressure (2-3 mm.). This in particular eliminated carbon tetrafluoride as a reaction product. It was just possible, however, that any carbon tetrafluoride which might have been formed by a disproportionation reaction involving two CF_3 radicals would react with the hot sodium in the carburetor on repeated recycling in the hydrogen stream. This possibility was examined as follows:

Carbon tetrafluoride at 84.0 mm. pressure was circulated over sodium maintained at 355°C. by a mercury boiler. No change in pressure was observed after 90 min. Since there appears to be no reaction between carbon tetrafluoride and sodium which does not result in a pressure decrease, this experiment was interpreted as indicating that sodium and carbon tetrafluoride would not react under the conditions of the experiments performed.

It was assumed, therefore, that in the sodium flame experiments, no product resulted which was not condensable in the liquid nitrogen traps, (*C*, Fig. 1).

(b) Condensable Products

Bulb *B*, containing the condensable products, was attached to a glass manifold

which was then evacuated. The glass break-off seal on the bulb was then opened by a magnetically-actuated hammer, and the gas distilled through a mercury cutoff into a calibrated storage volume, where its exact pressure at room temperature was recorded. At no time did the condensable products come into contact with stopcock lubricants. The gas sample was then fractionated at low temperature and pressure in an apparatus similar to that described by LeRoy (8). The temperature of the still was adjusted so that each fraction was removed at about 0.1 mm. pressure, and the removal of the fraction was deemed complete when the pressure dropped to 0.01 mm.

The distillation characteristics of the various fractions were compared with vapor pressures determined beforehand on the pure compounds which one would expect to find in the reaction products. Thus vapor pressure curves were previously made for pure samples of CF_3Cl , CF_3Br , CF_3I , CHF_3 , CH_2F_2 , CH_3F , C_2F_4 , and C_2F_6 .

Most of the analytical data were obtained in experiments in which CF_3I was reacted with atomic sodium. Unfortunately from the standpoint of analysis, the three main products, CHF_3 (when hydrogen was used as the carrier gas), C_2F_6 , and C_2F_4 , all have almost identical vapor pressure curves. Consequently, the distillation accomplished only the separation of these three products from the unreacted CF_3I . It was therefore necessary to pump off from the still sufficient of the reaction products to allow for a determination of the molecular weight of the gaseous solution by vapor density. The percentage of hexafluoroethane was then determined by absorbing the fluoroform and tetrafluoroethylene on a copper oxide - potassium hydroxide bead at 300°C . in the Blacet-Leighton apparatus. From the molecular weight and the percentage of hexafluoroethane, the total analysis could then be calculated. These analyses were checked by mass spectrometer analysis kindly performed for us by Dr. F. Lossing and Dr. A. Tickner, of the National Research Council.

(c) *Analysis of the Solid Reaction Products*

The deposit on the walls of the reaction tube was washed with water into a beaker. It consisted of a black, flaky, insoluble deposit as well as the expected white sodium halide. The weight of the black deposit was determined by filtering on a tared Gooch crucible and drying at 110°C . The sodium halide remained in solution in the filtrate. Iodide was precipitated with silver nitrate solution and determined gravimetrically, and the fluoride ion in the filtrate from the iodide precipitation determined as triphenyl tin fluoride. The carbon content of the black flaky material was determined by microanalytical methods.

Preparation of the Trifluoromethyl Halides

Iodotrifluoromethane was prepared by reacting carbon tetraiodide with iodine pentafluoride, according to the procedure described by Banks *et al.* (1). Good yields of CF_3I were obtained, and the purity was checked by molecular weight and vapor pressure determinations. The purity was in the order of 99.9%.

Bromotrifluoromethane was prepared by passing fluoroform and bromine through a tube at 600°C . and fractionating the product, a method described by Brice, Pearlson, and Simons (3). After fractionation on a Podbelniak column,

a product of about 99.5% purity was obtained. Chlorotrifluoromethane was prepared from difluorodichloromethane (Freon F-12), by passing it over anhydrous aluminum chloride at 150°C., and condensing the products in refrigerated traps (U.S. Patent No. 2,426,637, Sept. 2, 1947). After distillation of the products in the Podbelniak column, the purity was found to be about 99.3%.

EXPERIMENTAL RESULTS

(a) Experiments with Iodotrifluoromethane

In order to provide sufficient sodium vapor for these experiments, the sodium carburetor had to be heated at least to 275°C., and the reaction zone slightly higher (to avoid condensation of the sodium). Thus it was first necessary to ascertain that the iodotrifluoromethane would not pyrolyze under the experimental conditions. The first experiment therefore consisted of carrying out a run with CF_3I and hydrogen in the apparatus, but in the absence of sodium. The CF_3I went through the reactor quantitatively at 300°C., and fractionation proved that no pyrolysis had occurred.

Three runs were then performed with sodium in the carburetor, and with hydrogen as the carrier gas as follows (Table I).

TABLE I
EXPERIMENTAL OBSERVATIONS

	Run No.		
	6	7	25
Duration of run (min.)	275	306	154
Sodium temp. (°C.)	285	285	295
Reactor temp. (°C.)	285	285	295
Initial hydrogen pressure (mm. Hg)	2.34	2.56	2.32
Final hydrogen pressure (mm. Hg)	1.68	2.04	1.69
Initial hydrogen flow rate (moles/sec.) $\times 10^6$	33.2	39.5	41.8
Final hydrogen flow rate (moles/sec.) $\times 10^6$	19.3	31.4	21.8
Flame diameter (cm.)	2.0	2.0	2.0
P_{Na} (mm. Hg) $\times 10^5$	7.5	7.5	11.4
P_0 (mm. Hg) $\times 10^5$	2.0	2.0	2.0
$P_{\text{CF}_3\text{I}}$ (mm. Hg) $\times 10^5$	11.2	9.0	13.2
Diffusion constant (cm. ² /sec.)	980	804	902

Heller (6) established experimentally certain criteria which should be observed before the velocity constants of the sodium diffusion flame reactions could be regarded as valid. One of these was that the reaction zone, or flame, should not be smaller than 2.5 cm. The smaller flame diameter was used in these experiments because of the geometry of the apparatus; it was considered preferable to reduce the flame size rather than to increase the volume of the reactor or to allow the reaction zone to approach closer to the wall. Another of Heller's criteria was that v/δ , the ratio of the linear velocity of the carrier gas stream at the jet (in meters per second) to the diffusion constant of sodium in carrier gas-halide mixture, should be between 0.08 and 0.12. In all these experiments, this condition was observed—the value of v/δ was always about 0.08.

Under the experimental conditions recorded above, the values of the velocity constant of the primary reaction could be calculated (based on the assumption

here that all the sodium used up was consumed in the primary reaction). This calculation was performed, using the equation developed by von Hartel and Polanyi, viz.,

$$k = \left(\frac{\ln \frac{P_{\text{Na}}}{P_0}}{\frac{R-r}{R}} \right)^2 \frac{\delta}{P_{\text{CF}_3\text{I}}},$$

where k = velocity constant ($\text{cm}^3 \text{ molecules}^{-1} \text{ sec}^{-1}$),
 P_{Na} = partial pressure of sodium vapor (mm. Hg),
 P_0 = partial pressure of sodium vapor at the periphery of the flame (2×10^{-5} mm. Hg),
 R = radius of flame (cm.),
 r = radius of jet (cm.),
 δ = diffusion constant of sodium vapor in the carrier gas ($\text{cm}^2 \text{ sec}^{-1}$),
 $P_{\text{CF}_3\text{I}}$ = partial pressure of halide (mm. Hg).

For Runs No. 6, 7, and 25 respectively, values were found for the velocity constant of 1.8×10^{-10} , 1.8×10^{-10} , and $1.5 \times 10^{-10} \text{ cm}^3 \text{ moles}^{-1} \text{ sec}^{-1}$. Assuming a collision cross-sectional area (σ^2) of $3.5 \times 10^{-16} \text{ cm}^2$, Z , the collision number, can be calculated, and further assuming a steric factor of unity, the activation energy of the primary reaction was calculated to be 1.7, 1.7, and 1.9 kcal. per mole of halide in Runs No. 6, 7, and 25.

It was felt desirable to check as to whether or not the above assumptions were reasonable, by determining the activation energy of the primary reaction by finding the temperature coefficient of the velocity constant. In order to avoid secondary reaction of radicals with hydrogen, with an incidental decrease in carrier gas pressure, helium was used as the carrier gas. Although the diffusion constant of sodium vapor in helium is not known, it is evident that substitution of the experimental data in Polanyi's equation for the velocity constant would yield a numerical value of k/δ . By plotting $(\ln k - \ln \delta)$ against $1/T$, a straight line should result, whose slope would be the value of $-E/R$. A long series of such runs was made, but the values of k/δ obtained for such a rapid reaction were found to be erratic, and it was impossible to achieve accurate data using the rather narrow temperature range ($40^\circ\text{C}.$) obtainable with this apparatus. However, as described later, such experiments were feasible with slower reactions such as that between sodium and chlorotrifluoromethane, and these indicated that the activation energies calculated on the basis of observations at a single temperature were reasonably accurate.

A study of the quantities of reactants and products involved in four runs (No. 6, 7, 25, and 26) yields the information given in Table II.

The black flaky deposit was analyzed for Run No. 7 only, and was found to comprise 11 mole % of the reaction products. This material contained 73% C, and 5% H. The carbon dioxide shown in the analysis was an impurity; even triple distillation of the sodium failed to eliminate it completely from the system.

TABLE II
 ANALYSIS OF REACTION PRODUCTS

	Run No.			
	6	7	25	26
Carrier gas used	H ₂	H ₂	H ₂	He
Reactor temperature (°C.)	285	285	295	295
Moles CF ₃ I reacted (measured) × 10 ³	1.3	1.5	1.4	1.4
Moles NaI recovered from reactor × 10 ³	1.2	1.6	1.2	1.4
Gram-ions of F ⁻ recovered from reactor × 10 ⁴	13	11	4	6
Moles of C ₂ F ₄ in products × 10 ⁴	3.1	3.4	2.4	2.6
Moles of C ₂ F ₄ in products × 10 ⁵	14	19	4.8	9.7
Moles of CHF ₃ in products × 10 ⁵	12	14	9.5	nil
Moles of CO ₂ in products × 10 ⁵	20	25	2.5	2.9
Moles of CF ₃ I (unreacted) in products × 10 ⁴	5.5	6.9	4.3	6.0

A material balance drawn up for the reactants and products for Runs No. 6, 7, and 26 gives the results shown in Table III.

The analysis for fluoride ion in Run No. 25 was considered to be in error; the very dilute solution resulting from the washing down of the reactor was allowed to stand for several days before being analyzed, a procedure almost certain to result in a low figure for fluoride ion. In the other three experiments, however, analysis was carried out immediately after each run was completed.

From the foregoing table it will be seen that for Runs No. 6 and 7, where hydrogen was used as the carrier gas, all of the materials entering the reactor can be satisfactorily accounted for. With helium, however, the quantity of fluoride ion in the solid products in the reactor was low; in these runs a yellow deposit always formed in the first cold trap wherever a layer of mercury was present. This yellow material was identified as mercurous fluoride. The exact role played by hydrogen which results in the retention of fluoride ion in the reactor is not obvious; the drop in hydrogen pressure could not possibly account for all of the fluoride recovered.

(b) *Experiments with Bromotrifluoromethane*

Diffusion flame experiments were performed with CF₃Br, and the activation energy of the reaction calculated for observations at a single temperature by the method described in the previous section. Assuming that the primary reaction is that between atomic sodium and the bromine, the activation energy amounts

 TABLE III
 MASS BALANCES

	Run No.		
	6	7	26
Gram-atoms of fluorine entering reactor × 10 ³	3.9	4.5	4.2
Gram-atoms of fluorine found in products × 10 ³	3.9	4.3	2.6
Gram-atoms of iodine entering reactor × 10 ³	1.3	1.5	1.4
Gram-atoms of iodine found in products × 10 ³	1.2	1.6	1.4
Gram-atoms of carbon entering reactor		1.5 × 10 ⁻³	
Gram-atoms of carbon found in products		1.5 × 10 ⁻³	

to 2.3 kcal. per mole. No analysis of products could be undertaken, for it was found that CF_3Br has vapor pressure characteristics very similar to C_2F_6 , C_2F_4 , and CHF_3 .

(c) *Experiments with Chlorotrifluoromethane*

Three runs were made with chlorotrifluoromethane, using hydrogen as the carrier gas, under the conditions given in Table IV.

TABLE IV
EXPERIMENTAL CONDITIONS

Run No.	Sodium temp. ($^{\circ}\text{C}.$)	Reactor temp. ($^{\circ}\text{C}.$)
28	295	295
29	275	275
30	285	315

Assuming a steric factor of unity and a collision cross section of $3.5 \times 10^{-15} \text{ cm}^2$ the activation energy of the primary reaction was calculated to be 7.4, 7.5, and 6.9 kcal. per mole, using data from Runs No. 28, 29, and 30 respectively. Evaluation of the slope of a plot of $\ln k$ against $1/T$ (where k = velocity constant, and T the reactor temperature) will give a value for the activation energy which will, however, be independent of the two assumptions. Such a plot was made, using the following data (Table V).

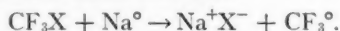
TABLE V
VELOCITY CONSTANTS AS A FUNCTION OF TEMPERATURE

Run No.	k ($\text{cm}^3 \text{ moles}^{-1} \text{ sec}^{-1}$)	$1/T$
29	3.85×10^{11}	1.83×10^{-3}
28	5.55×10^{11}	1.76×10^{-3}
30	1.02×10^{12}	1.70×10^{-3}

The slope of the best straight line to fit the above data gave an activation energy of 7.0 kcal. per mole. Accordingly, it was felt that values assumed for the steric factor and collision cross sections do result in a reasonably accurate figure for the value of the activation energy when calculated from an observation at a single temperature.

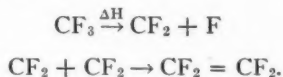
DISCUSSION OF RESULTS

In all sodium flame experiments involving more than one kind of halogen atom attached to alkyl carbon, there is always some doubt as to whether the sodium atoms will react exclusively with the proper halogen atom. For instance, in the foregoing experiments there is no certainty that some reaction would not occur between atomic sodium and fluoride. If this reaction between sodium and fluoride were appreciable, however, one would not expect to find much difference between the reaction rates of CF_3I and CF_3Cl with sodium. Because the reaction rates did differ so widely, the conclusion has been drawn that in the flame reactions studied, the primary reaction was indeed



It is almost certain that trifluoromethyl radicals were present in the tube, as evidenced by the hexafluoroethane and fluoroform in the products—the former from the combination of two trifluoromethyl radicals, and the latter from reaction between trifluoromethyl and hydrogen.

Several alternatives suggest themselves for explaining the presence of tetrafluoroethylene in the products. It could result from the thermal decomposition of a trifluoromethyl radical:



The disproportionation reaction, $\text{CF}_3 + \text{CF}_3 \rightarrow \text{CF}_2 + \text{CF}_4$, was ruled out by the absence of carbon tetrafluoride in the products. However, the reaction $\text{CF}_3 + \text{CF}_3 \rightarrow \text{C}_2\text{F}_4 + \text{F}_2$ is a possibility.

In the case of the very fast reactions, such as that involving the iodotrifluoromethane, there is severe impoverishment of the halide reactant in the flame zone, creating a reasonable probability of reaction between sodium and trifluoromethyl radicals, which would almost certainly give rise to tetrafluoroethylene. Unless this reaction started a chain reaction which resulted in the deposition of carbon in the tube, it could have occurred to a maximum of about 20%.

Because the reactions with the iodo- and bromo-trifluoroethylene were so rapid (the collision yield for the former is about one-fifth), the assumption that the concentration of the halide in the flame zone is constant is not tenable; this violates one of the conditions under which the equation used for the evaluation of the rate constant is valid, and thus the values given for the activation energies of these fast reactions must be regarded as approximate only. The effect of variations in the halide partial pressure in the flame zone have been studied by Cvetanović and LeRoy (4). Another assumption about which there may be some doubt is that δ , the diffusion constant of sodium, varies directly with the absolute temperature. No attempt will be made here to adjust the values obtained by using the simple equation for the rate constant, to allow for these divergences from ideal conditions.

The possibility of secondary reactions made the interpretation of the analytical data difficult; on the other hand, the employment of this technique made it possible to compare the relative reactivities of iodo-, bromo-, and chloro-trifluoromethane, giving values lower than those accepted for the corresponding methyl halides.

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NORMAL AND CROSS-LINKED POLYSTYRENE

I. HUGGINS' k' AS A MEASURE OF NONLINEARITY¹

By J. A. MANSON AND L. H. CRAGG

ABSTRACT

Polystyrene polymerized in emulsion at 55°C. to near-complete conversion has been subjected to careful primary, secondary, and tertiary fractionation. For representative samples and fractions thereof, the intrinsic viscosity $[\eta]$ and the slope constants β and k' have been determined at 25°C. in butanone and benzene. For intrinsic viscosities in benzene ranging from 2.10 to 8.37, the equation $\log [\eta]$ (in benzene) = $0.31 + 1.23 \log [\eta]$ (in butanone) holds. In butanone the value of k' is 0.40 ± 0.01 , changing from 0.39 for the lower fractions ($[\eta]$ in butanone < 2.00) to 0.41 for the highest fractions; in benzene, the better solvent, the corresponding values of k' are 0.02 units lower.

Samples of cross-linked polystyrene were prepared by copolymerizing styrene with small proportions of divinylbenzene. Values of k' determined for the soluble cross-linked species, both unfractionated and fractionated, varied (in butanone) all the way from the normal 0.40 to 1.14, depending on the proportion of divinylbenzene used.

It is concluded that k' is a sensitive indicator of nonlinearity in polymer molecules, and that in polystyrene as normally prepared in emulsion systems the molecules are essentially linear.

INTRODUCTION

In preparation for studies of the influence of molecular weight on various solution properties of polystyrene, it was necessary to separate a sample of polystyrene into fractions that differed only in molecular weight and were each as nearly homogeneous with respect to molecular weight as possible. By far the most convenient means of accomplishing this end was the familiar fractional precipitation technique (8) which exploits differences in solubility due to differences in molecular weight. But the solubility of polymers is affected by composition (23) and by molecular structure (13) as well as by molecular weight, and hence a given fraction obtained by fractional precipitation might actually be heterogeneous with respect to all three. In polystyrene, differences in composition may be neglected (the effect of end-groups on composition being important only in very low polymers), but structural heterogeneities might well be significant (24). In polystyrene formed all at the same temperature the most important of these structural differences should be that due to branching (or cross-linking) arising from a chain transfer reaction involving free radicals and polymer chains (15, p. 60). Bamford and Dewar (3) believe that in any sample of polystyrene prepared to high conversion, branched species would be present, and in such amount as to leave open to criticism many published equations relating intrinsic viscosity to molecular weight. It was important, therefore, to determine whether or not such branching had occurred in our polymerization.

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Based on a thesis submitted in partial fulfillment of the requirements for the degree of Master of Science, April, 1951. Results of this investigation were reported at the Canadian High Polymer Forum in Ottawa, June, 1950.

Unfortunately, no accepted method for detecting and measuring branching was available. The ratio of viscosity-average molecular weight to osmotic-average molecular weight, often used for this purpose, is much too sensitive to molecular-weight heterogeneity. Insolubility in a variety of solvents is evidence of *extensive* cross-linking (15, p. 65), and when cross-linking renders a polymer insoluble, the swelling ratio (4, 14) is a satisfactory measure of its degree, but this method is inapplicable to nonlinear species that are soluble—the ones in which we are primarily interested.

There was, however, accumulating evidence that the Huggins' slope constant k' (21) might serve as a means of detecting branching. On theoretical grounds, Simha (31) had shown that k' should be higher for branched species. Speiser and Whittenberger (33) had found that k' was much higher for amylopectin, the branched form of starch, than for amylose, the linear form. Baker (2) had shown that for soluble cross-linked species—"microgel"—in polybutadiene the inherent-viscosity slope was positive (and therefore k' was higher than for linear species). Morrison, Holmes, and McIntosh (27) had noted that when polyvinyl acetate was aged under conditions that might be expected to encourage cross-linking the value of k' increased slightly. Mochel *et al.* (26), working with Neoprene GN, and Henderson and Legge (18), and Cragg and Switzer (9), working with GR-S (polybutadiene-co-styrene), had attributed similar anomalous viscosity behavior of "top" fractions to the presence of branched species. Perhaps the most conclusive evidence was that of Walker and Winkler (37) who, having prepared lightly cross-linked polystyrene by copolymerizing styrene and divinylbenzene, found for soluble fractions values of k' as high as 0.80 (as compared with 0.38 for the normal polystyrene). They concluded that the normal polystyrene molecule was essentially linear in structure.

On the other hand, Janssen (22) had found perfectly normal values of k' for the fractions obtained from polystyrene copolymerized with the cross-linking agent di-isopropylidiphenyl. Because of this apparent disagreement, and because both of these investigations with cross-linked polystyrene had been limited to bulk-polymerized samples, it seemed wise to make a similar investigation using materials prepared in emulsion, and at the same time to make a thorough study of the usefulness of k' as an indicator of nonlinearity in polymer molecules.

EXPERIMENTAL

1. Apparatus

Polymerizations were carried out at $55.0 (\pm 0.2)^{\circ}\text{C}$. in 250-ml. glass-stoppered bottles. The bottles, clamped in a motor-driven steel frame, were rotated end-over-end in the constant-temperature bath at a rate of 33 r.p.m.

Temperatures required for fractionation and intrinsic-viscosity determinations were maintained in glass constant-temperature baths regulated to $45.0 (\pm 0.2)^{\circ}\text{C}$. and $25.0 (\pm 0.02)^{\circ}\text{C}$., respectively.

A most convenient vessel for primary fractionations was found to be a 3-liter separatory funnel with its stem cut short, and fitted with a stopper providing for a glycerine-sealed paddle stirrer and a vacuum outlet. For subsequent

fractionations, other separatory funnels of appropriate sizes were used. With a separatory funnel, the coacervate may be drawn off quite neatly and easily, provided great care has been taken to keep the stopcock vacuum-tight.

The viscometers used, U14-3 and U14-11 of a modified Ubbelohde series, had a large bulb to permit the making of dilutions in the viscometer itself. Designed to have negligible kinetic-energy corrections (19), these viscometers gave almost identical intrinsic viscosity values (within ± 0.02 units) for a given polystyrene solution. Specially-designed viscometer clamps were used to ensure that the viscometers were mounted in a standard position each time they were used.

2. Materials

(a) Solvents and Nonsolvents

Benzene.—(Steel Company of Canada), ASTM Industrial Grade, redistilled and dried over sodium; b.p. 80.5°C ., $n_D^{25} = 1.4972$.

Toluene.—(Steel Company of Canada), Nitration Grade, treated with concentrated sulphuric acid to remove sulphur compounds, redistilled and dried over sodium; b.p. 110°C ., $n_D^{25} = 1.4926$.

Ethanol.—(Canadian Industrial Alcohol Company), unmatured spirits, 95%.

1-Butanol.—(Baker and Adamson), Technical Grade, 95%.

Butanone.—(Shell Oil Company), Technical Grade, dried over calcium chloride and redistilled; b.p. 79.8°C ., $n_D^{25} = 1.3754$.

Since variations of refractive index, flow time, and solvent power have been noted for various samples of purified solvents, particularly butanone (11), the refractive indices and flow times of the solvents were checked frequently, and a given "batch" of solvent was used throughout a given series of intrinsic viscosity determinations.

(b) Reagents

Styrene.—(Polymer Corporation of Canada), inhibited with *t*-butylcatechol.

Divinylbenzene.—(Polymer Corporation of Canada), 50% solution in ethylbenzene.

Potassium persulphate, dodecyl mercaptan, and soap flakes.—(Obtained from Polymer Corporation of Canada).

3. Preparation of Polymers

(a) Linear Polystyrene

Samples were prepared by polymerizing, at 55°C ., an emulsion having the following composition (except for certain variations in the proportion of mercaptan which are noted in Table I):

Styrene (washed with 10% sodium hydroxide)	50.0 gm.
Oxygen-free distilled water	90.0 gm.
Soap flakes	2.5 gm.
Potassium persulphate	0.15 gm.
Dodecyl mercaptan	0.025 ml.

After the reactants had been mixed in an atmosphere of nitrogen in the 250-ml. bottles, the resulting emulsion was rotated in the bottles at 55°C. until the desired percentage conversion was reached. Coagulation of the final mixture by pouring into an excess of ethanol yielded a granular polymer which was filtered off, washed with ethanol, and dried at 50°C. for from 15 to 20 hr.

(b) *Cross-linked Polystyrene*

Preparation of the cross-linked polymer was carried out in the same manner as that of the linear polystyrene, except that varying amounts of divinylbenzene were added to the emulsion. Although drying was effected under the same conditions as used for the linear polystyrene, the dried samples were fractionated as soon as possible to minimize any variations in molecular weight caused by further reaction after precipitation.

4. Fractionation

The method of fractional precipitation by preferential evaporation of solvent from a solution of a polymer in a solvent-nonsolvent mixture was found to be convenient and efficient. It has been used by Badgley, Frilette, and Mark (1), Goldberg, Hohenstein, and Mark (16), and by Gralén and Lagermalm (17) and leads to a distribution curve similar to that obtained with the same polymer by other conventional precipitation methods.

Following the procedure of Goldberg *et al.* (16), a 3% solution of polystyrene in a mixture of butanone and 1-butanol was used. (Initial concentrations not greater than 1% are commonly recommended but higher concentrations are permissible when the primary fractions are to be refractionated.)

Just enough butanol was added slowly with stirring to a solution of the polymer in butanone to bring the solution to the precipitation point, as judged by the obscuring of the filament of an incandescent lamp placed behind the bath. The volume required was about 50% by volume of the original volume; this made the concentration at initial precipitation 2%.

After just enough butanone had been added to reclarify the mixture, suction was applied and butanone was evaporated until it was judged that a precipitate of the desired size would form. The mixture was then stirred for 30 min. to ensure the attainment of equilibrium, and allowed to stand until phase separation was complete. After removal of the coacervate (or precipitated fraction) suction was applied once more, and the procedure repeated as above to yield the second, third, and subsequent fractions.

Reprecipitation of the polymer by pouring the coacervate into an excess of 1-butanol or ethanol—an operation which, according to Scott (30), should remove the lower molecular-weight "tail" accompanying each fraction—yielded a fibrous, fluffy fraction. This was recovered by filtration, washed with water, and partially dried at room temperature.

These *primary* fractions were each refractionated; resulting *secondary* fractions having similar intrinsic viscosities were then combined and refractionated. The final *tertiary* fractions were carefully dried at 50°C. to constant weight. Furth-

er fractionation failed to effect any consistent improvement in the fractions detectable by intrinsic viscosity measurement.

5. Intrinsic Viscosity Determinations

Preparation of Solutions

Solutions were prepared by allowing the necessary weight of polystyrene to stand away from direct light in a 50-ml. volumetric flask with solvent at room temperature until equilibrium was reached. To loosen swollen coalescing particles, the contents of the flasks were swirled gently (36), but not shaken vigorously. If, as with cross-linked polystyrene, all the solid did not dissolve, only the soluble portion was used for the intrinsic-viscosity determinations. If all the polymer was soluble the solutions were diluted to 50 ml. with solvent at 25.0°C. and filtered through a coarse sintered-glass disk to remove dust. If some solid remained undissolved, the soluble portion was decanted, filtered, and made up to volume at 25.0°C. To minimize the amount of dust, flasks used for the final solutions were boiled in concentrated nitric acid, rinsed with filtered distilled water, and dried at 110°C.

Concentration Determinations

Since with tertiary fractions there was no significant change in concentration after filtration, concentrations were calculated directly from the amount of polymer weighed out. On the other hand, with preliminary fractions, which frequently contain considerable dust, concentrations had to be determined by evaporation of aliquot samples of solution at 50°C. to constant weight. Tests proved the latter method to be accurate and precise to $\pm 1\%$. Concentrations were calculated either directly in gm. solute per 100 ml. solution, or by multiplying the weight per cent (gm. solute per 100 gm. solution) by the density of the solution at the temperature desired.

Flow Times

Flow times were measured in duplicate, or, more usually, in triplicate (or, if flow times remained reasonably constant, until agreement to $\pm 1\%$ was obtained). With concentrated solutions in butanone of high molecular weight fractions or even with more dilute solutions in benzene, the flow times were too high and hence too irregular to yield the maximum precision of $\pm 1\%$.

Calculation of Intrinsic Flow Time, or Intrinsic Viscosity

Values of intrinsic flow time, $[t]$, were determined by graphical extrapolation using values of inherent flow time, $(\ln t_r)/c$, at three or four concentrations ranging from 0.4 to 0.005%, or from 0.2% for the high molecular weight fractions. Inherent flow time was used instead of the more usual reduced flow time, $(t_r - 1)/c$ (or t_{sp}/c), because the curves were often more nearly linear and always had a smaller slope, and hence (1) the extrapolation could be made with greater confidence, and (2) the plotting could be more conveniently done on a scale that would give precise values of $[t]$. Because both kinetic energy effects in the viscometers and the variation of the density of the solutions with concentration were shown to be negligible, $\eta_r = t_r$ and therefore $\ln \eta_r/c = \ln t_r/c$, $\eta_{sp}/c = t_{sp}/c$, and $[\eta] = [t]$. Accordingly, in what follows "viscosity" will be used in place of "flow time" in referring to all such functions.

k' and Its Determination

In the equation of Huggins (21)

$$(1) \quad \frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c,$$

k' is an empirical slope constant. It corresponds to the constant β in the equation of Mead and Fuoss (25)

$$(2) \quad \frac{\ln \eta_r}{c} = [\eta] - \beta[\eta]^2 c.$$

At very low concentrations the curves η_{sp}/c vs. c and $(\ln \eta_r)/c$ vs. c are linear: and if k' and β are evaluated from the limiting slopes ($c \rightarrow 0$) of Equations (1) and (2), they must be related by the equation

$$(3) \quad k' = A - \beta,$$

where $A = 0.50$ (12). In practice the slopes determined are those of curves drawn through points derived from measurements at *finite* concentrations. Under these conditions Equation (3) may not be strictly valid (35). Because of the nature of the curves, however, it is more convenient to determine β and to compute k' from it. The values of k' were obtained in this way and are therefore subject to any systematic error introduced by assuming the validity of Equation (3). This error should, however, be small, and particularly since we are interested in *differences* between values of k' , should not affect the conclusions.

RESULTS

1. Normal Polystyrene

The intrinsic viscosity, $[\eta]$, the slope of the inherent viscosity-concentration line, $\frac{\Delta(\ln \eta_r)/c}{\Delta c}$, and values of the slope constants, β and k' , were determined for unfractionated samples of polystyrene, for representative primary, secondary, and tertiary fractions in butanone (MEK), and for tertiary fractions in benzene as well. A selection of these data is given in Tables I, II, and III.

TABLE I
VISCOSITY DATA FOR UNFRACTIONATED POLYSTYRENE SAMPLES AND FOR TYPICAL
PRIMARY AND SECONDARY FRACTIONS IN BUTANONE AT 25°C:

Sample Code No.*	% Conversion (orig. sample)	$[\eta]$	- Slope	β	k'
C	96	2.04	0.45 ₀	0.11	0.39
B1	97	1.96	0.42 ₅	0.11	0.39
C1	96	2.82	0.72 ₄	0.09	0.41
C4	96	1.48	0.28 ₀	0.13	0.37
D1	30	1.63	0.30 ₀	0.11	0.39
C2C	96	1.24	0.18 ₅	0.12	0.38
C4A	96	1.37	0.17 ₅	0.09	0.41
D1A	30	2.00	0.42 ₅	0.11	0.39

*The first letter refers to the batch of polystyrene: B - 0.050% modifier and 97% conversion, C - 0.025% modifier and 96% conversion, D - 0.025% modifier and 30% conversion, F (later tables) - 0.025% modifier and 96% conversion. The numbers and second letters identify the fractions: thus D1 is the first primary fraction from batch D, and C4A is the first secondary fraction from the fourth primary fraction from batch C.

TABLE II
 VISCOSITY DATA FOR TYPICAL TERTIARY POLYSTYRENE FRACTIONS IN BUTANONE AT 25°C.

Sample* Code No.	Concentration, gm./100 ml. soln.	$\frac{\ln \eta_r}{c}$	$[\eta]$	— Slope	β	k'
C1A1	0.467	3.09	3.55	1.11	0.09	0.41
	0.233	3.33				
	0.156	3.38				
	0.117	3.42				
C2A1	0.436	2.49	2.82	0.75 ₀	0.10	0.40
	0.218	2.66				
	0.145	2.72				
	0.109	2.78				
C4A3	0.424	0.97	1.00	0.08 ₀	0.08	0.42
	0.212	0.99				
	0.141	0.98				
	0.106	0.98				
C4B2	0.383	0.66	0.69	0.08 ₀	0.17	0.33
	0.192	0.67				
	0.128	0.69				
	0.096	0.69				
F1A1	0.426	2.50	2.80	0.72 ₅	0.09	0.41
	0.213	2.64				
	0.142	2.68				
	0.107	2.72				
F3A2	0.421	1.24	1.31	0.16 ₀	0.09	0.41
	0.210	1.28				
	0.140	1.29				
F3A3	0.413	1.11	1.19	0.19 ₀	0.13	0.37
	0.206	1.14				
	0.138	1.15				
	0.103	1.17				
F3C1	0.374	0.74	0.77	0.10 ₀	0.17	0.33
	0.187	0.75				
	0.125	0.77				
F3C2	0.388	0.59	0.59	—	—	—
	0.194	0.59				
	0.129	0.60				
F5A1	0.415	1.86	2.01	0.35 ₀	0.09	0.41
	0.208	1.94				
	0.138	1.95				
	0.104	1.97				
F5A3	0.385	1.23	1.26	0.15 ₀	0.09	0.41
	0.193	1.25				
	0.128	1.26				
F7B1	0.370	1.32	1.39	0.19 ₀	0.10	0.40
	0.185	1.35				
	0.123	1.36				
	0.092	1.36				
F7B2	0.381	1.15	1.21	0.14 ₀	0.10	0.40
	0.190	1.18				
	0.127	1.18				
	0.095	1.19				
F7B3	0.378	0.99	1.03	0.11 ₀	0.10	0.40
	0.189	1.01				
	0.126	1.02				

*The second numeral gives the order in which the tertiary fraction precipitated. Since tertiary fractions were obtained from samples obtained by combining secondary fractions of similar intrinsic viscosity, the first part of the code refers to the major constituent of this combined secondary fraction.

TABLE III
 VISCOSITY DATA FOR TERTIARY POLYSTYRENE FRACTIONS IN BENZENE AT 25°C.

Sample Code No.	$[\eta]$	- Slope	β	k'
C1A1	8.37	7.6	0.11	0.39
C2A1	6.39	4.7	0.12	0.38
C4A3	2.06	0.60	0.14	0.36
C4B2	1.36	0.40	0.20	0.30
F1A1	6.33	5.1	0.13	0.37
F3A2	4.37	2.4	0.12	0.38
F3A3	2.87	1.1	0.14	0.36
F3C1	1.58	0.40	0.16	0.34
F3C2	1.12	0.25	0.20	0.30
F5A1	4.44	2.7	0.14	0.36
F5A3	2.80	1.2	0.16	0.34
F7B1	2.95	1.4	0.16	0.34
F7B2	2.71	0.98	0.13	0.37
F7B3	2.10	0.73	0.17	0.33

In Fig. 1 are drawn some representative inherent viscosity curves of the type used in obtaining $[\eta]$ and β . These serve to indicate the precision of the derived data. Because the experimental points never lie exactly on any one straight line, a choice of the "best" line must be made. This leads to uncertainty both in the intercept and in the slope.

The uncertainty in $[\eta]$ is fairly slight, usually being of the order of ± 0.01 . Additional evidence for the rather good precision of the intrinsic viscosity values is given in Fig. 2 in which values of $\log [\eta]$ determined in benzene are plotted against those determined in butanone. The points for fractions of normal polystyrene fall on or close to a straight line (with one exception). Incidentally,

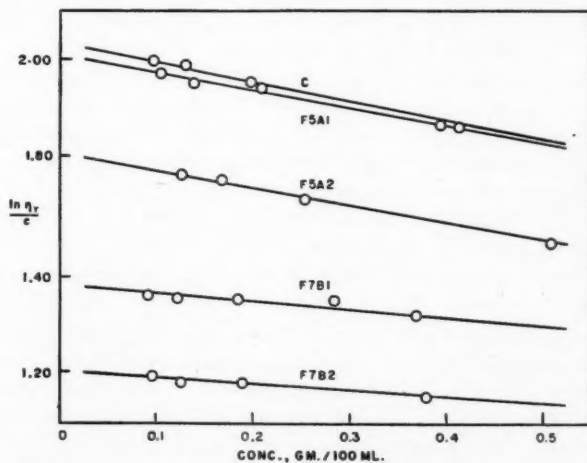


FIG. 1. Some representative inherent viscosity-concentration curves for normal polystyrene in butanone. (Note that the ordinate scale is interrupted.)

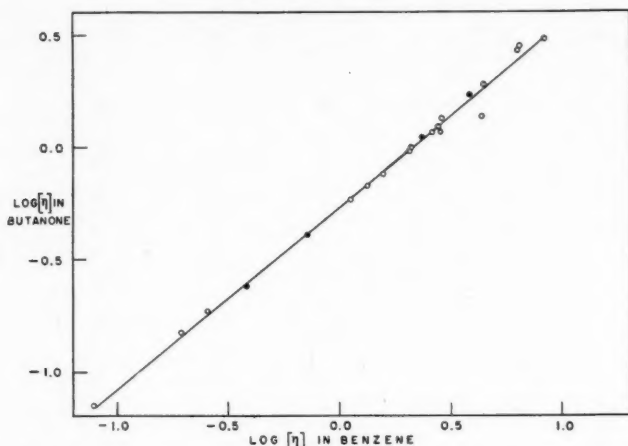


FIG. 2. Relation between intrinsic viscosities of normal polystyrene fractions in benzene and butanone.

○ This paper. • Bawn, Freeman, and Kamaliddin (6).

the equation for this straight line, $\log [\eta] \text{ (in benzene)} = 0.31 + 1.23 \log [\eta] \text{ (in butanone)}$, agrees remarkably well with the one obtained by Bawn, Freeman, and Kamaliddin (6)— $\log [\eta] \text{ (in benzene)} = 0.33 + 1.23 \log [\eta] \text{ (in butanone)}$.

The uncertainty in the value of the slope is more serious, and since in calculating β this uncertainty is added to that in the *square* of the intrinsic viscosity, it is little wonder that the precision of β values is relatively low, particularly for the low molecular weight fractions. This lack of precision is evident in Tables I, II and III, but it may be shown more clearly by means of a suitable graph. In Fig. 3, typical values of the slope are plotted against corresponding values of $[\eta]^2$ and the limits of error in the slope (corresponding to the lines that differ most in slope and yet could be considered as drawn "through" the points on the $(\ln \eta_r)/c$ vs. c plot) are indicated by vertical lines. If for all these samples β were identical, the points should all be on a straight line through the origin and of slope equal to β . Two such lines corresponding to different values of β are drawn. It is clear that in butanone the value $\beta = 0.10 \pm 0.01$ (which corresponds to $k' = 0.40 \pm 0.01$) fits all the samples within the experimental error but it is also clear that any single determination might lead to quite a different value, particularly in the low molecular weight range, where the precision is much lower.

Similar considerations apply to the values of the slope, of β , and of k' derived from measurements in benzene. They are probably somewhat less precise than the values in butanone, but again the data can be combined to give a representative value more trustworthy than that obtained from any single determination (particularly from any at low intrinsic viscosities). From our data the "best" value for β with benzene as solvent appears to be 0.12 ± 0.01 and for k' , 0.38 ± 0.01 .

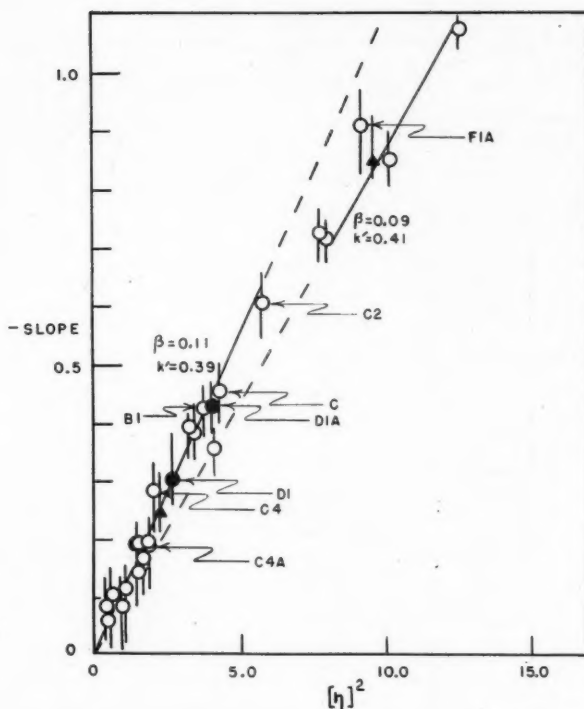


FIG. 3. Relation between slope of inherent viscosity-concentration curves and intrinsic viscosities for polystyrene in butanone.

- Normal, 96% conversion.
- Normal, 30% conversion.
- ▲ Cross-linked (0.0030% DVB), 96% conversion.

2. Cross-linked Polystyrene

The data for various samples of cross-linked polystyrene, prepared by copolymerizing styrene with various small proportions of divinylbenzene (DVB), are given in Table IV. The measurements were made in butanone at 25.0°C.; similar measurements were made using benzene as solvent.

Two effects of the introduction of cross-links are immediately evident: the intrinsic viscosity is markedly decreased and values of the slope constants, β and k' , are markedly increased. It should be emphasized that all the viscosity measurements were made with solutions from which any insoluble gel had been removed by filtration. The values of $[\eta]$, β , and k' are therefore those of soluble species. Moreover, although insoluble gel did not form unless the proportion of divinylbenzene in this polymerization recipe was 0.1% or more, the effect of one-fourth this amount of cross-linking agent was sufficient to change the slope of the inherent viscosity curve from negative to positive and to change k' from the normal 0.40 to 0.61.

TABLE IV
 VISCOSITY DATA FOR UNFRACTIONATED CROSS-LINKED POLYSTYRENE IN BUTANONE
 AT 25.0°C.

$\frac{\% \text{ DVB}}{(\text{wt. DVB} \times 100)} \text{ wt. styrene}$	Concentration, gm./100 ml. soln.	$\frac{\ln \eta}{c}$	$[\eta]$	Slope	β	k'
0.00300	0.386	2.19	2.38	- 0.48	0.09	0.41
	0.193	2.28				
	0.129	2.32				
	0.097	2.32				
0.00625	0.404	2.28	2.55	- 0.68	0.10	0.40
	0.202	2.42				
	0.135	2.46				
	0.101	2.48				
0.0125	0.400	1.74	1.82	- 0.20	0.06	0.44
	0.200	1.80				
	0.133	1.80				
	0.100	1.78				
0.0250	0.418	1.00	0.96	0.09 _s	- 0.11	0.61
	0.209	0.97				
	0.139	0.96				
	0.105	0.96				
0.0500	0.392	0.68 ₄	0.63	0.12 _s	- 0.31	0.81
	0.196	0.65 _s				
	0.131	0.64 _s				
	0.098	0.62 ₇				
0.100	0.392	0.38 _s	0.34	0.12 _s	- 0.64	1.14
	0.196	0.37 ₂				
	0.131	0.36 ₄				
	0.098	0.34 _s				
0.120	0.376	0.34 _s	0.32	0.01 _s	- 0.49	0.99
	0.188	0.33 ₁				
	0.125	0.31 ₇				
	0.094	0.31 ₃				
0.140	0.432	0.29 ₁	0.29	0.02 _s	- 0.30	0.80
	0.216	0.30 ₆				
	0.144	0.29 ₆				
0.150	0.460	0.26 ₆	0.26	0.01	- 0.15	0.65
	0.230	0.27 ₆				
	0.153	0.26 ₄				

In the unfractionated samples some of the molecules will be larger and more cross-linked than others. These should concentrate in the first fractions obtained by fractional precipitation. Samples of cross-linked polystyrene containing 0.0030%, 0.0125%, 0.0250%, and 0.0500% divinylbenzene were subjected to a primary fractionation and the viscosity measurements made with the top three fractions from each. Data for the fractions from the sample containing 0.0125% divinylbenzene are given in Table V.

The results are in accord with expectation. The small amount of cross-linking that was responsible for the increase in k' from 0.40 for normal polystyrene to 0.44 for the unfractionated cross-linked material is apparently present largely

TABLE V
 VISCOSITY DATA FOR PRIMARY FRACTIONS OF CROSS-LINKED POLYSTYRENE (0.0125%
 DVB) IN BUTANONE AT 25.0°C.

Fraction Code No.	Concentration, gm./100 ml. soln.	$\frac{\ln \eta_r}{c}$	$[\eta]$	Slope	β	k'
J1	0.416	2.68	2.61	0.13	-0.02	0.52
	0.208	2.66				
	0.139	2.63				
	0.104	2.63				
J2	0.420	2.46	2.46	0.00	0.00	0.50
	0.210	2.46				
	0.140	2.46				
	0.105	2.45				
J3	0.417	1.32	1.40	-0.28	0.10	0.40
	0.209	1.36				
	0.139	1.37				
	0.104	1.38				

in the two top fractions where it is sufficient to cause an increase in k' of 0.12 and 0.10 units, a difference much larger than the experimental error of determining k' .

The effect of different degrees of cross-linking on the k' of fractions is clearly shown in Fig. 4 where the data are plotted in such a way as to facilitate comparison. The dotted lines indicate what the slope of the inherent viscosity-concentration line would have been had the sample been free of cross-linking (i.e., $\beta = 0.10$). If the data are plotted as in Fig. 5 (compare Fig. 3), the effect

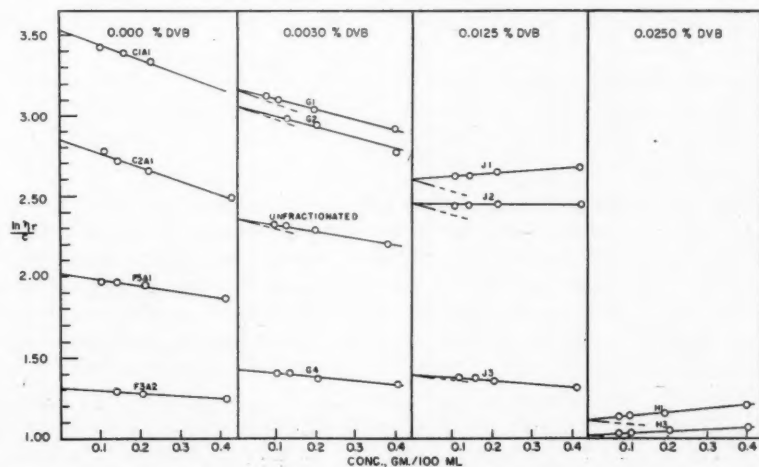


FIG. 4. Inherent viscosity-concentration curves for normal and cross-linked polystyrene in butanone.

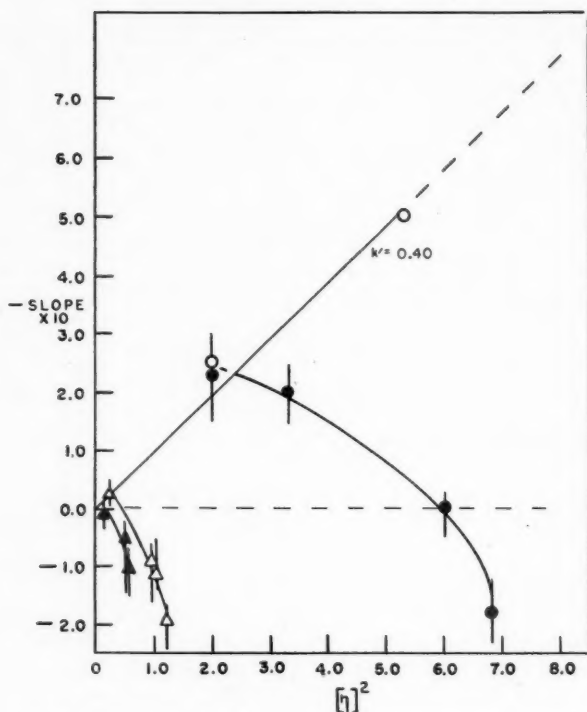


FIG. 5. Relation between slope of inherent viscosity-concentration curves and intrinsic viscosities for cross-linked polystyrene in butanone.

○ 0.0030% DVB. • 0.0125% DVB. △ 0.0250% DVB. ▲ 0.0500% DVB.

of cross-linking on slope (and therefore on β and k') is shown even more dramatically. The greater the proportion of divinylbenzene in the polymer the lower is the intrinsic viscosity at which anomalous values of slope, of β , and of k' appear.

DISCUSSION

From the results presented it is evident that k' is a measure of nonlinearity in polymer molecules and, for polystyrene at least, a sensitive one. An unmistakable increase in k' is caused by the introduction of very small proportions of a cross-linking agent, so small indeed that there is on the average only one cross-link for every 10,000 mers in the polymer chain. Cross-linking to such a slight degree should have the same effect on the physical behavior of the polymer as branching.

In other words, nonlinearity—no matter what its origin—could be detected by measurements of k' . Normal polystyrene must, then, contain no significant amount of branched or cross-linked species, because for even the highest molecular weight fractions the value of k' is normal. Our evidence was obtained with emulsion-polymerized polystyrene, but a similar conclusion was reached by

Walker and Winkler (37) from experiments with bulk-polymerized polystyrene. More recently the conclusion that polystyrene is essentially linear in structure has been supported by the light-scattering experiments of Outer, Carr, and Zimm (28).

Our evidence suggests strongly that k' is independent of the degree of molecular-weight heterogeneity of the sample. For example, from Table I, the value of k' for unfractionated material is 0.39 and the average value for primary fractions is 0.39, both of which values agree within experimental error with the best value for tertiary fractions, 0.40 ± 0.01 . (See also Fig. 3.) A similar conclusion has been reached by Davis (10). On the other hand, Spencer and Boyer (34), Coppick (7), and Howlett, Minshall, and Urquhart (20) contend that molecular-weight heterogeneity does affect the slope of the viscosity curves. It may well be that the effect they observed was really due to structural heterogeneity. Certainly for a polymer sample containing branched species in significant proportion the k' will be higher than for the fractions consisting of linear species alone. For example, k' for the unfractionated copolymer of polystyrene and divinylbenzene (0.0125%) was 0.44, smaller than that for its two top fractions, which presumably contained most of the branched species, but greater than the 0.40 of linear polystyrene fractions.

Again, the k' of polystyrene does not seem to be affected by the degree of conversion obtained in the polymerization (nor by changes in the proportion of modifier used in the recipe). Evidence for this conclusion is in Table I and Fig. 3. Bamford and Dewar (3) warned that branching must be expected in polystyrene polymerized to high conversion. If our primary conclusion, that k' is a sensitive indicator of nonlinearity of polymer molecules, is correct, then the secondary conclusion follows that branching does not occur to any significant degree in polystyrene polymerized to any conversion, high or low, in emulsion at 55°C.

Thirdly, our data affords further precise evidence that k' depends on the solvent, the value for the good solvent benzene (0.38) being smaller than that for the poorer solvent butanone (0.40). This effect, for which Bawn (5) and Palit, Colombo, and Mark (29) have recently supplied much more striking evidence, is in accord with the theoretical predictions of Simha (31), and others.

Finally, it is clear that k' changes little if at all with molecular weight. When Huggins first proposed his equation, he stated that k' was independent of molecular weight and this claim has since received abundant experimental support (see, for example, Bawn (5)). There is some indication in our data that k' is not *completely* independent of molecular weight but increases very slightly with increasing chain length. Thus in butanone at 25°C. the best value seems to be 0.39 in the lower range of molecular weights (that is, for fractions with intrinsic viscosity, in butanone at 25°C., of less than 2.00) changing gradually to 0.41 for the fractions of highest molecular weight. Similarly, the value in benzene seems to change from 0.37 to 0.39. This effect, assuming it to be real,* is not

*The higher value of k' was observed with fractions of such high molecular weight that rate-of-shear effects might be large enough to affect k' . A careful study of the effect of rate-of-shear on the intrinsic viscosity and slope constants of these and other fractions is being made in this laboratory.

unexpected (32, Part II, p. 75). For very high molecular weight polymers a given solvent should be "poorer" than for low molecular weight polymers and hence k' should be greater for the former. Since changing from the good solvent benzene to the fairly poor solvent butanone causes a change in k' of only 0.02 units it is to be expected that this effect (of molecular weight on solvent power and hence on k') would be small.

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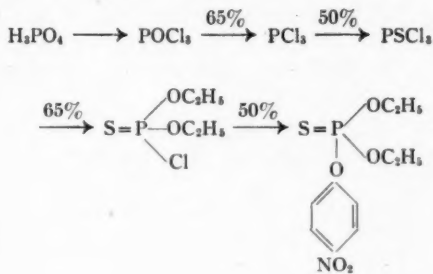
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NOTES

Synthesis of P^{32} Labeled Parathion

The wide use of Parathion (0,0-diethyl-0-*p*-nitrophenyl thiophosphate) (5) as an insecticide indicates the probable usefulness of the labeled compound in investigations of insect toxicology. P^{32} has been introduced through a modification of a synthesis previously reported (3) according to



Labeled phosphorus oxychloride was prepared by two methods: (a) $\text{Ag}_3\text{P}^{32}\text{O}_4$, prepared from $\text{Na}_2\text{HP}^{32}\text{O}_4$; (1) was heated with PCl_5 in a sealed tube at 130° for 10 min. (2). (b) PCl_5 was added slowly to anhydrous $\text{H}_3\text{P}^{32}\text{O}_4$. After the solution was allowed to stand for 48 hr., quantitative yields of $\text{P}^{32}\text{OCl}_3$ were obtained on distillation.



Labeled phosphorus oxychloride obtained by either method was reduced on passage over carbon granules at 1000°C . to yield P^{32}Cl_3 (65%) which on reaction with S in a sealed tube (4) at 150° for two hours gave $\text{P}^{32}\text{SCl}_3$ (53%). This was combined with sodium ethylate and the resulting diethoxy thiophosphoryl chloride reacted with an aqueous solution of sodium *p*-nitrophenolate (3) to yield Parathion (16% based on PCl_3).

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The Reduction of Some Chlorinated Azobenzenes with Titanous Sulphate

Knecht and Hibbert (1) have shown that azo groups are quantitatively reduced by titanous chloride according to the following reaction scheme:—



This method has been widely used, and has been found satisfactory for a large variety of azo compounds especially azo dyes.

On attempting to utilize this method for the analysis of some chlorinated azobenzenes, it was found that the above generalized reaction does not always apply. Reduction of 2,2'-dichloroazobenzene and 3,3'-dichloroazobenzene with titanous sulphate required only two equivalents instead of the expected four. (See Table I.)

TABLE I
MOLES TITANOUS SULPHATE CONSUMED PER MOLE AZO COMPOUND REDUCED

Compound	Moles Ti^{+++} consumed per mole of compound
Azobenzene	2.00 ± 0.04 (av. of 6 determinations)
Hydrazobenzene	Nil
2,2'-Dichloroazobenzene	2.05 ± 0.03 (av. of 3 determinations)
3,3'-Dichloroazobenzene	2.04 ± 0.05 (av. of 4 determinations)
4,4'-Dichloroazobenzene	3.27 ± 0.02 (av. of 4 determinations)

To investigate this anomaly, additional experiments were conducted with azobenzene as well as the chlorinated azobenzenes. The products resulting from the reduction with titanous sulphate were isolated and were found to be benzidine rather than aniline type compounds. It was believed that this was caused by a benzidine rearrangement of the intermediate hydrazo compound. The strongly acid medium under which the reduction takes place would certainly favor such a rearrangement.

To confirm this hypothesis it was shown that when the para positions of azobenzenes are blocked so that rearrangement cannot take place, the reduction with titanous sulphate proceeds normally. Thus, with 4,4'-dichloroazobenzene it was found that nearly four equivalents of titanous sulphate were consumed. Attempts to reduce pure hydrazobenzene with titanous sulphate also confirmed that such compounds undergo rearrangement and are not reduced under these reaction conditions.

While this work was being carried out, it was reported by Veibel (3) that some azo compounds are rearranged into benzidine during titration with titanous chloride and consume only two equivalents of this latter compound. Veibel (4) offers as partial proof the fact that, after the reaction is completed, addition of sodium nitrite to the solution, and subsequent coupling with β -naphthol, yields a dye the color of which is characteristic of benzidine and not aniline.

In all of the above work, the method of reduction was similar to that used by Siggia (2). For isolation of the reaction products the compounds (1 gm.) were

dissolved in ethanol (100 ml.), then 20 ml. of $\frac{1}{2}N$ titanous sulphate was added, together with 50 ml. of concentrated hydrochloric acid. After the mixture was refluxed for 10 min., it was cooled and diluted with water (200 ml.). The hydrochloride salt crystallized out on standing. This was filtered off, and then hydrolyzed to the free base by means of sodium hydroxide or pyridene. After recrystallization, the free base was identified by its melting point. In one case the identity of the compound was confirmed by preparing the benzene sulphonamide derivative.

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